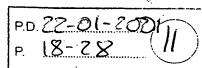


XP008008679

Laser diode (LD) imagings and photopolymers for LD imagings

Toshiyuki Urano

Mitsubishi Chemical Corp. Research Center, 1000 Kamoshida Aoba-ku Yokohama 227, urano@atlas.rc.m-kagaku.co.jp



ABSTRACT

The laser photopolymers and the laser imaging systems equipped with various laser diodes such as 410nm-Violet laser, 532nm-frequency-doubled laser and high-power-infrared laser are presented. The photopolymer's performances in sensitivity, resolution and safelight character dependent on the wavelength and power of laser light are discussed.

1. INTRODUCTION

Rapid development of laser diode (LD) is changing the laser imaging systems in graphic arts, especially laser-printing-plate systems. 10 years ago, the laser-plate-imaging systems using a 532nm-frequency-doubled yag laser (FD Yag laser)

which is pumped by laser diode, were predominant 5 years ago, 830nm-high-power infrared lasers was applied to the laser-plate-imaging systems. Recently, the new systems equipped with a 410nm-low power-Violet laser are exhibited by 6 manufacturers. The specially designed photopolymers for the laser imaging systems have been developed to afford high sensitivity, resolution and safelight character. The conventional-plate-making systems using a mask and the laser-plate making system equipped with a FD-Yag laser are depicted in Fig. 1. The required sensitivity of the laser plate for FD-Yag laser is ca. 0.1 mJcm⁻², which is ca. 10000 times higher than that of the conventional plate. The high-speed photopolymer is a key technology for laser-printing-plate systems

2. SPECTRAL SENSITIVITY

Fig. 2 shows the spectral sensitivity of photopolymers and the laser emission wavelength. The power for FD-Yag laser (532 nm) is 50-100 mW, Violet laser (410 nm) is 5 - 30 mW and IR laser (832 nm and 1064 nm) is 1 - 40 W. The radical photopolymerization systems are applied to the FD-Yag laser plate and Violet laser plate as negative laser plates [1], and the polymer phase-transfer systems are applied to IR laser plate as a positive plate [2].

3. LASER SETTER

The laser plate is generally exposed by a scanning of ca. 10μ m laser spot (resolution 1000 - 4000 dpi and 0.5 - 10 min / m²). Figs. 3-5. Show the tree different exposure systems (laser setters) for laser plates. The outer and inner drum type laser setters (Figs. 3 and 4, respectively) provide high-resolution photopolymer images on the plates, and are used for

Laser Applications in Microelectronic and Optoelectronic Manufacturing VI, Malcolm C. Gower, Henry Helvajian, Koji Sugloka, Jan J. Dubowski, Editors, Proceedings of SPIE Vol. 4274 (2001) © 2001 SPIE - 0277-786X/01/\$15.00

PEST AVAILABLE COP

4Ω

high quality printings such as commercial color printings. The flatbed-type-laser setter (Fig. 5) is suitable for2 high-speed-plate making such as news paper printings. The performances of lasers and characters of photoplymers are summarized in Table. 1.

4. NEGATIVE LASER PLATE

4-1. FD-Yag laser plate

The power of FD-Yag laser is rather low (50 – 200 mW). Thus the required sensitivity is $50 - 200 \,\mu$ Jcm² at 532 nm. Mitsubishi Chemical Corp. (MCC) is the first maker in Japan supplying FD-Yag laser plates 1994. The plate-making systems using the FD-Yag laser have been improved over 6 years in respect to exposure speed (producibility) and stability in image-formation, and the systems become a mature technology. The combinations of FD-Yag laser plates and flatbed laser setters are applied to newspaper printings due to the high producibility, however the systems have a disadvantage in safelight character. FD-Yag laser plates need a safelight condition of dark orange.

4-2. Violet laser plate

The power of Violet laser is very low (5-30 mW). The required sensitivity is $15-30 \,\mu$ Jcm⁻² at 410 nm. MCC demonstrated platemakings using MCC's-violet-laser plates first in the world May 2000. Violet-laser-plate-making system has two advantages. One is ignorable amount of maintenance fee due to cheap violet lasers, and the other is yellow-safelight character.

As for the sensitivity of Violet laser plate, the sensitivity is almost same as an ultimate sensitivity of photopolymer obtained from a permeating rate of oxygen (2.1×10^{13} molecules/cm²s) through 2 μ m-thick poly(vinylalcohol) (PVA) layer as an oxygen-barrier layer as depicted in Fig.6. Bird et al. theoretically estimated the ultimate sensitivity as the light energy (13.2μ Jcm⁻²), which provides the condition for photopolymer-image-forming; the radical polymerization is higher than radical trapping by oxygen permeated through PVA layer [3].

Double Amplifying Photoinitiator (DAP) technology, to increase the sensitivity of photoplymer to near ultimate sensitivity, MCC developed new photoinitiator systems (DAP). We consider the mechanism of the photoinitiator as a scheme in Fig. 7. Sensitizer dyes (SD) sensitizedly decompose Radical generators (RR), emitting radicals (R.). The radicals (R.) additionally react to acrylate monomers (M), forming acrylate monomer and polymer radicals (M.). The radicals (M.) undergo induced decomposition of SD and RR, emitting more active radicals S. and R. In the photoinitiator system, the photopolymer is doubly accelerated by the photochemical dye-sensitization (sensitization 1) and the induced decomposition of RR and SR (sensitization 2), affording the near ultimate sensitivity.

5. POSITIVE IR LASER PLATE

The power of IR laser is significantly high. The required sensitivity is 100 - 200 mJcm⁻² at 832 and 1064 nm. MCC demonstrated platemakings using MCC's-IR-laser plates first in Japan 1997. IR-laser-plate-making system has advantages of the good reproducibility of photopolymer image, and the white-safelight character. The plate is constructed by an aluminum-printing substrate and a 2μ m photopolymer layer on the substrate containing binder

polymers and dyes as a IR light absorbent. The photopolymer images are formed by the photo-thermal conversion and subsequent-polymer-phase transfer.

Photopolymer nano-structure controlled (PNSC) technology [2], Fig. 9 shows the temperature distribution in the photopolymer layer of 2 μ m thickness at the exposure of 10 μ m beam spot from 832 nm IR laser (7.6 W) (Fig. 8). Since the thermal conductivity of aluminum substrate is ca. Three order of magnitude higher than photopolymer, the temperature of photopolymer at near surface (facing air) and near substrate can be simulated as ca. 1000 and 500 °C, respectively. Considering the distribution of temperature in the photopolymer layer at laser exposure, we established the technology of controlling a hydrogen-bonding matrix in the photopolymer layer against the thickness (Z coordination in Fig. 8.) from surface to the substrate by applying a particular-physical treatment to afford much higher density of matrix at near surface than that at near substrate (Fig. 10). The high-density matrix is insoluble against an alkaline developer. In the spot exposure by IR laser, the matrix is turned to be the low-density matrix by instantaneous heat, and then positive images are formed. The degree of the matrix density is directly observed from a dynamic DSC (DDSC) as a response change of signal at a frequency as depicted in Fig. 11 [2].

In the image reproducibility of IR laser plate, Fig. 12 schematically exhibits the distribution of light intensity in IR laser spot and the comparison of the spot image of IR positive-laser plate to that of negative laser plates. There exist a discreet threshold of light intensity in the image-formation by IR laser. Since the image-formation by IR laser is governed by not photochemical but photophysical reactions such as the photo-thermal conversion and the phase transfer of polymer binders, the IR laser plate has only sensitivity at high-intensity-light exposure such as laser spots, and no sensitivity against week-intensity light such as room lights. Moreover the image-formation of IR laser plate is not influenced by a halation reflected on the substrate and a background laser light, so then higher reproducibility of image is achieved compared to negative laser plates.

6. IMAGE SAMPLES

Fig. 13 exhibits a photograph of sharp positive image (200 lpi 50% screen) of IR laser plate formed by a scanning exposure of 2400 dpi. Figs. 14 and 15 shows other application examples of the FD-Yag-laser photopolymers. SEM photograph of resist image formed on copper substrate (Fig. 14), and ink cells (175 lpi screen) formed on gravure printing cylinder using copper-etching photoresists. The technologies of laser photopolymer are attractive for not only graphic-arts application but also other applications such as holography image and memory, 3 D manufacturing and microelectronics.

References

- 1. H. Nagasaka, T. Urano and M. Tsuchiyama,"New Efficient Photo-radical-initiator Systems for Visible Light and their Photo-initiation Mechanism," Mitsubishi Kasei R and D, 1, pp.52-60, 1992.
- T. Urano and H. Tomiyasu, Thermal CTP vs. Violet CTP, Japan Printer, 11,pp. 19-23, 2000.

Proc. SPIE Vol. 4274

3. G. R. Bird, W. D.Pandolfe, S. Shimizu, "The Ultimate Capabilities of Organic Imaging Systems," *Photogr. Sci. En.* 3, pp.122-128, 1978.

Table.1. Laser printing plates and performances of laser setter

	Visible laser		IR laser
	Violet laser (410nm)	FD-YAG laser(532nm)	(832, 1064nm)
Laser power	5-30 mW	50-200 mW	1-40W
Exposure speed	3-10min/m ²	0.5-10min/m ²	3-10min/m ²
resolution	1000-4000 dpi	1000-4000 dpi	1000-4000 dpi
Reproducibility of small-dot image at 2500 dpi	Spot of 20 μ m diameter	Spot of 25 μ m diameter	Spot of 15 μ m diameter
Sensitivity of laser plate	15 – 30 μ Jcm ⁻²	50-200 μ Jcm ⁻²	100-200mJ cm ⁻²
Imaging material of laser plate	Radical polymerization	Radical polymerization	Polymer phase- transfer
Image of laser plate	Negative	Negative	ositive
Safty light	Yellow light	Dark Orange light	
			hite light

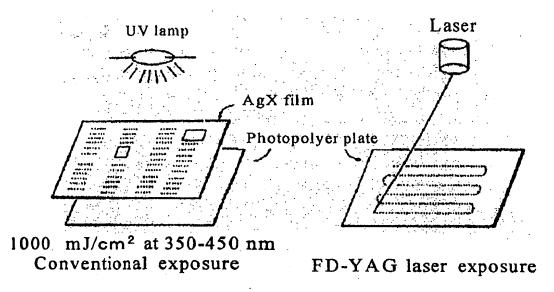


Figure 1. Exposure systems and required sensitivity

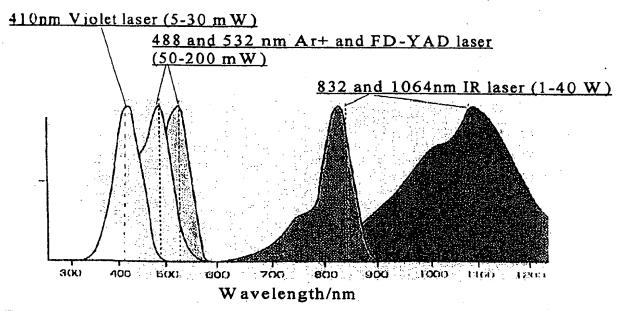


Figure 2: Spectral sensitivity.

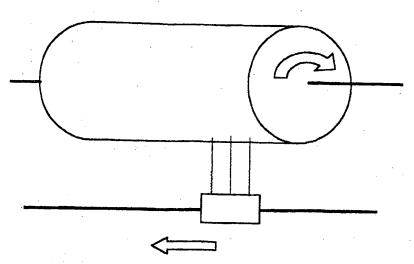


Figure 3: Outer drum laser setter.

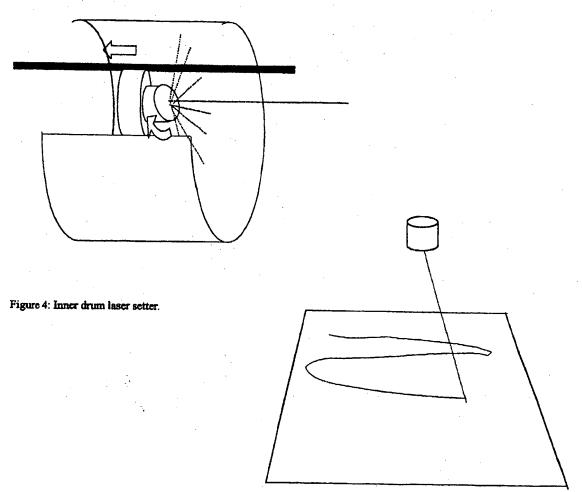


Figure 5: Flatbed laser setter

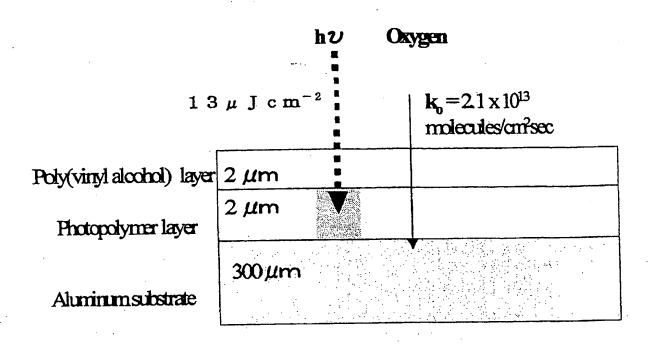
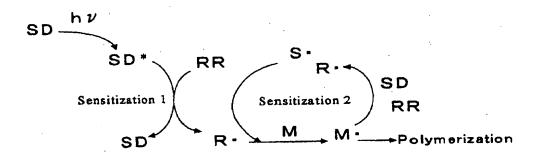


Figure 6: Ultimate sensitivity of photopolymer.

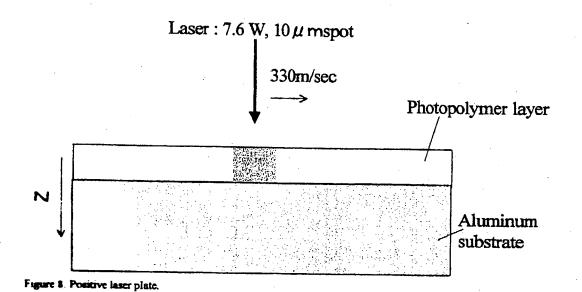


SD:sensitizer dye S:Dye radical SD:photoexcited sensitizer dye

RR: radical generator R: radical from RR M: acrylate monomer

M -: acrylate monomer radicals

Figure 7: DAP technology.



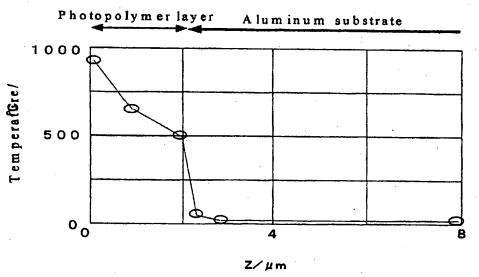


Figure 9: Temperature distribution against depth (Z) in IR laser plate.

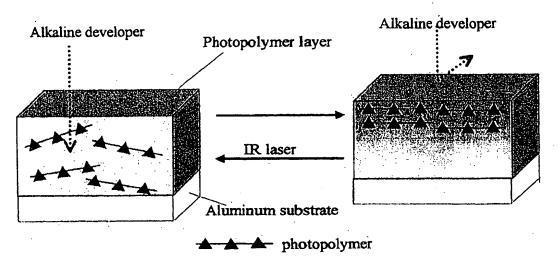


Figure 10: PNSC technology in positive laser plate.

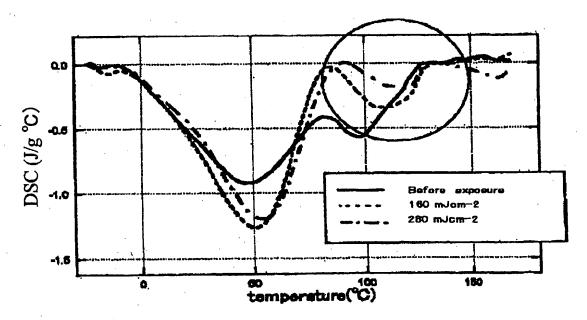


Figure 11: Dynamic DSC at 0.002 Hz and 5 °C/min.

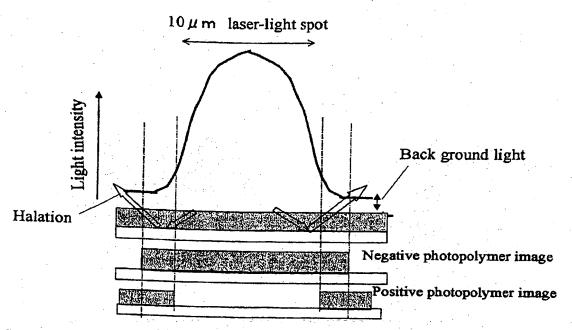


Figure 12: Distribution of light intensity in laser-beam spot on plate surface and photoplymer spot image.

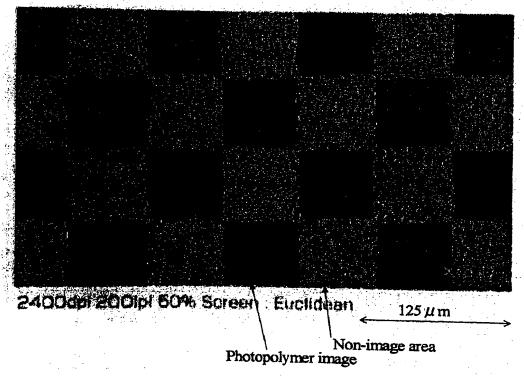
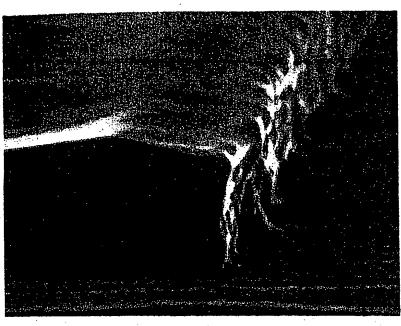
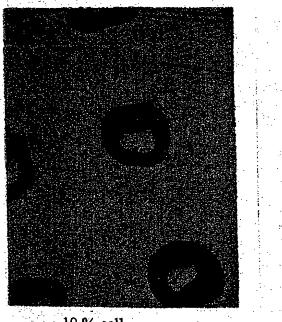


Figure 13: Image of printing plate.

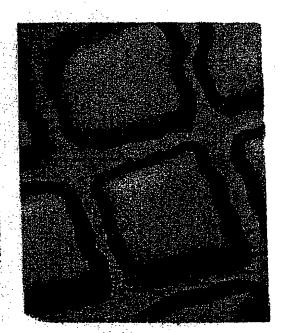


3 µ m

Figure 14: Resist pattern of laser photopolymer.



10 % cell



65 % cell

Figure 15: Copper-etching-resist images fabricated using laser photopolymer.

150 µm

THIS PAGE BLANK (USPTO)

This Page is Inserted by IFW Indexing and Scanning Operations and is not part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

BLACK BORDERS

IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

FADED TEXT OR DRAWING

BLURRED OR ILLEGIBLE TEXT OR DRAWING

SKEWED/SLANTED IMAGES

COLOR OR BLACK AND WHITE PHOTOGRAPHS

GRAY SCALE DOCUMENTS

LINES OR MARKS ON ORIGINAL DOCUMENT

REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

IMAGES ARE BEST AVAILABLE COPY.

☐ OTHER:

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.